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The IR spectra were recorded on a UR-20 spectrophotometer in chloroform (for compounds IIa-e) and in carbon tetrachloride (for IIIa-d). The PMR spectra were run on a RYa-2310 spectrometer (60 MHz), using HMDS as internal standard. The UV spectra were recorded on a SF-16 spectrophotometer for $1 \cdot 10^{-4}$ mole/liter solutions. The constants of the basic (for compounds IIa-d and IIIa, c) and acidic (for IIa) ionization in a sulfuric acid–water or sodium hydroxide–water system were determined spectrophotometrically on the same apparatus at 20 ± 1°C. The analytical wave-length corresponded to the basic ionization of compounds (IIa-d at 306 nm, compounds IIIa, c at 315 nm, and for acidic ionization at 365 nm. The $pK_{ap.a.}^{zw}$ and $pK_{ap.s.}^{zw}$ values were calculated from seven points at a given reliability of 0.98 according to formulas given in [6]. The yields, physical constants, and analytical data of the compounds obtained are listed in Table 1.

3-Aroyl-6-methyl-2-oxopyridines (IIa-e). A 0.05 mole portion of 3-aroyl-6-methyl-2-methoxypyridine (Ia-e) in 20 ml of 10% hydrochloric acid is boiled for 4 h. The mixture is cooled, the precipitate is separated and crystallized from ethanol.

3-Aroyl-1,6-dimethyl-2-oxopyridines (IIIa-d). A solution of 0.014 mole of potassium hydroxide in 8 ml of water and 5 ml of methyl iodide are added to a solution of 0.01 mole of compound II in 30 ml of ethanol. The mixture is boiled for 2 h, the solvent and excess of methyl iodide are distilled, and the residue is crystallized from water.

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SYNTHESIS AND ACID-BASE TRANSFORMATIONS OF (4-STYRYLPYRIDINIO)-ALKANESULFONATES

O. S. Éikher-Lorka and G.-K. K. Kupyatis

UDC 547.829'822.6:543.422.6

(4-Styrylpyridinio)alkanesulfonates were synthesized by condensation of 2-(4-methylpyridinio)- and 2-(4-ethylpyridinio)-1-ethanesulfonates with aromatic aldehydes, and also by quaternization of 4-styrylpyridine by sulfoalkylating agents. For the p- and o-hydroxystyrylpyridinium compounds in aqueous solutions, the pK_a values were determined spectrophotometrically. It is believed that the planarity of the o-hydroxypyridinium compounds is disturbed because of the reaction of the hydroxy and the α-sulfonatomethyl groups.

It is known that pyridylsulfobetaines [1] and also unsaturated quaternary pyridine salts [2] are used in galvanotechniques. The possibility was examined of using stilbazoles as antioxidants and antitumorigenic preparations [3], and also as solvent polarity indicators [4]. We synthesized quaternary pyridinium salts containing a sulfo group and a double bond

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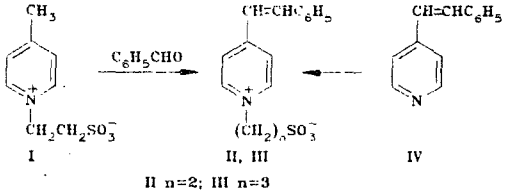
TABLE 1. Characteristics of Styrylpyridinium Compounds

Compound	R	R^1	R^2	mp, °C (decomp.)	λ_{max}, nm, pH ≤ 6 (pH ≥ 11)	Empirical formula	Yield, %
II	—	—	—	344—345	346	$C_{15}H_{15}NO_3S$	73 (А) 54 (Б)
III	—	—	—	247—248	346	$C_{16}H_{17}NO_3S$	72
X	H	OH	H	310—311	298	$C_{14}H_{13}NO_4S$	5
XI	H	OCH_3	H	316—317	298	$C_{15}H_{15}NO_4S$	5
XII	C_2H_5	OH	H	317—318	360 (433)	$C_{16}H_{17}NO_4S$	42
XIII	C_2H_5	H	OH	227—228	341 (433)	$C_{16}H_{17}NO_4S$	78
XIV	C_2H_5	OH	OH	228—229	368	$C_{16}H_{17}NO_5S$	10
XV	C_2H_5	$N(CH_3)_2$	H	278—279	428	$C_{18}H_{22}N_2O_3S$	34
XVI	CH_2CH_2OH	H	H	285—287	325	$C_{16}H_{17}NO_4S$	27
XVII	CH_2CH_2OH	OH	H	308—309	363 (436)	$C_{16}H_{17}NO_5S$	59
XVIII	CH_2CH_2OH	H	OH	265—266	355 (433)	$C_{16}H_{17}NO_5S$	82
XIX	CH_2CH_2OH	OCH_3	H	276—277	359	$C_{17}H_{19}NO_5S$	58
XX	CH_2CH_2OH	Cl	H	263—264	328	$C_{16}H_{16}ClNO_4S$	17
XXI	$CH_2CH(OH)CH_2OH$	H	H	209—210	326	$C_{17}H_{19}NO_5S$	28
XXII	C_2H_5	OH	H	246—247	360 (433)	$C_{16}H_{16}NNaO_4S$	96
XXIII	C_2H_5	H	OH	203—205	341 (433)	$C_{16}H_{16}NNaO_4S$	95

[a]For compounds XII, XIII, XVII, XVIII, the following pK_α values were found spectrophotometrically: 8.70; 8.60; 8.76; 8.58, respectively.

in side chains. 2-(4-Styrylpyridinio)ethanesulfonate (II) was synthesized by two methods: condenstation of 2-(4-methylpyridinio)ethanesulfonate (I) with benzaldehyde and quaternization of 4-styrylpyridine (IV) by sodium β-bromoethanesulfonate in an ethylene glycol solution. 3-(4-Styrylpyridinio)propanesulfonate (III) was obtained by quaternization of 4-styrylpyridine (IV) with its 1,3-propane sultone in acetonitrile (Tables 1, 2).

Sulfobetaines VII-IX were synthesized by the quaternization of sodium 2-(4-pyridyl)-ethanesulfonate (V) by ethyl bromide, ethylene chlorohydrin and glycerin α-monochlorohydrin. They, as well as 2-(4-pyridyl)ethanesulfonic acid (VI), were further condensed with substituted benzaldehydes.



The sodium salt (V) has an absorption band at 1605 cm^{-1} in the IR spectrum, while in the IR spectrum of acid VI this band is absent and an absorption band appears at 1635 cm^{-1}. Using the data in [5, 6] as a basis, we assigned the first band to the C=N group vibrations, and the second to $C=\overset{+}{N}$ in the pyridine ring. In the PMR spectra (D_2O), the α-protons of the pyridine ring give signals in the form of doublets for compounds V-VII, respectively, with a shift at 8.44, 8.69, 8.66 ppm, and the β-protons — at 7.33, 8.00, 7.90 pp, respectively. It is seen that the signals of the pyridine ring protons of compounds VI and VII almost coincide, and are present in a weaker field than the signals of base V. From these data we concluded that 2-(4-pyridyl)ethanesulfonic acid exists in the form of a sulfobetaine (VI). Despite this, its condensation with 4-hydroxy- and 4-methoxybenzaldehydes was successfully accompolished only in absolute DMSO at elevated temperature (110°C) in the presence of an equivalent amount of piperidine. The yield of the desired end products X and XI was only 5%.

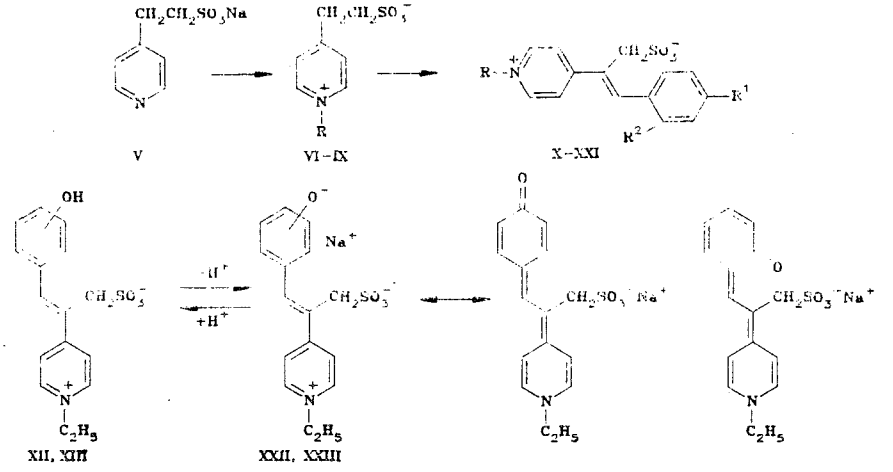
The condensation of sulfobetaines VII-IX with substituted benzaldehydes was carried out in a mixture of absolute ethanol with absolute DMSO (4:1) in the presence of piperidine. The use of absolute ethanol alone as the solvent decreases the yields nearly by half. The presence and the nature of the substituents in the substituted benzaldehydes also noticeably influence the course of the reaction. In the presence of electron-donor hydroxy and methoxy groups, sulfobetaines XII, XIII, XVII-XIX were synthesized in a 42-82% yield. An exception

TABLE 2. Chemical Shifts of Styrylpyridinium Protons (δ, ppm)

Compound	N—Alk	$CH_2SO_3^-$ (s)	H—Py (d)[b]		—CH= (s)	$C_6H_3R^1R^2$ [c]
			2-H	3-H		
II	4,67 t; 3,06 t	—	8,78	8,02	7,82—7,07	
III	4,58 t; 2,38 m; 2,16 t	—	8,84	8,11	8,02—7,24	
X	—	3,98	8,61	8,09	7,26	7,64 d; 6,69 d
XI	—	4,01	8,64	8,12	7,33	7,78 d; 6,88 d; 3,71 s
XII	4,44 q; 1,43 t	4,00	8,77	8,18	7,36	7,70 d; 6,71 d
XIII	4,46 q; 1,42 t	4,02	8,78	8,12	7,33	7,22—6,62
XIV	4,48 q; 1,44 t	4,02	8,80	8,15	7,40	8,13—7,95 6.36—6,13
XV	4,49 q; 1,66 t	4,42	8,64	8,13	7,56	7,79 d; 6,93 d; 3,09 s
XVI	4,47 t; 3,72 t	4,02	8,73	8,19	7,84—7,69; 7,44—7,22	
XVII	4,44 t; 3,70 t	4,02	8,67	8,17	7,37	7,69 d; 6,72 d
XVIII	4,44 t; 3,71 t	4,01	8,67	8,11	7,33	8,08—7,73; 7,20—6,56
XIX	4,44 t; 3,72 t	3,99	8,67	8,17	7,38	7,77 d; 6,86 d; 3,98 s
XX	4,47 t; 3,71 t	3,98	8,71	8,07	7,33	7,79 d; 7,33 d
XXI	4,49 d; 3,87 m; 3,44 d	4,00	8,65	8,16	7,96—7,67; 7,44—7,13	
XXII	4,52 q; 1,66 t	4,52	8,54	8,08	7,56	7,67 d; 6,72 d
XXIII	4,51 q; 1,60 t	4,51	8,69	8,13	7,56	7,98—7,89; 7,40—7,22; 7,13—6,89

[a] Compounds XV, XXII, XXIII were dissolved in a 1:1 CD_3CN—D_2O mixture, the remaining compounds were dissolved in $(CD_3)_2SO$.
[b] J_{23} = 6 Hz.
[c] For para-substituted compounds J_{23} = 8 Hz.

was only the reaction with 2,4-dihydroxybenzaldehyde where, because of the resinification of the reaction mixture and the difficulties which this presents during the purification of the product, the yield of the sulfobetaine XIV was only 10%. In the presence of an electron acceptor substituent, or in the absence of substituents, the yields of sulfobetaines XVI, XX, XXI were lower, being equal to 17-28% (Table 1). Despite the fact that the SO_3^- group is electron-accepting and should increase the acidity of the CH_2 group protons, our reactions were carried out under more rigid conditions than the condensations of quaternary salts of γ-picoline with the corresponding benzaldehydes [7, 8]. This can be explained by the poor solubility of sulfobetaines VI-IX in absolute solvents.



XII, XXII — p-substituted XIII, XXIII — o-substituted VI, X, XI R=H; VII, XII—XV R=C_2H_5; VIII, XVI—XX R=CH_2CH_2OH; IX, XXI R=$CH_2CH(OH)CH_2OH$; R^1 and R^2 see Table 1

The hydroxy-substituted sulfobetaines XII and XIII were converted by reaction with sodium hydroxide into anhydro-bases XXII, XXIII in yields of 95-96%. In the study of electronic absorption spectra of compounds XII, XIII, XVII, XVIII in neutral and alkaline media, it was found that the transition from para-substituted to ortho-substituted compounds leads to a hypsochromic shift of the principal band of the π,π*-transitions, which indicates a disturbance of the planarity of the molecules and decrease in the resonance interaction of the aromatic and heterocyclic rings [7]. This is evident only in the phenol forms, i.e., in a

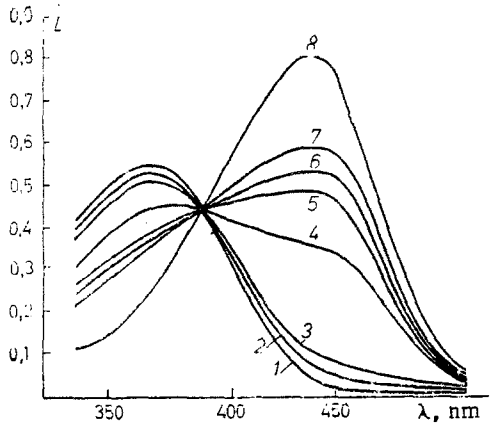


Fig. 1. Absorption spectra of compound XII at different pH values of the medium. 1) 6.5; 2) 7.3; 3) 7.72; 4) 8.50; 5) 8.77; 6) 8.90; 7) 9.03; 8) 10.04.

neutral medium, and can happen only because of an interaction of the ortho-OH group with the SO_3^- group (Table 1). When the absorption spectra of quaternary salts of styrylpyridines XII, XIII, XV-XIX were compared with those of analogous compounds, previously synthesized by other authors, which have a CH_3 group [7] or H [7, 8] instead of the $CH_2SO_3^-$ group, it was found that the bulky $CH_2SO_3^-$ group disturbs the planarity of the molecule and hypsochromically shifts the absorption band of the π,π^*-transitions approximately in the same way the CH_3 group (Table 1).

We determined the acidity constants of the phenol groups in compounds XII, XIII, XVII, XVIII spectrophotometrically. Figure 1 shows the absorption spectra of 3-(4-hydroxyphenyl)-2-(1-ethyl-4-pyridinio)-2-propenesulfonate (XII) at different pH. The spectra of monohydroxy-substituted sulfobetaines at different pH have a sharply expressed isobestic point, which indicates the binarity of the system. p,o-Dihydroxystyrylpyridiniosulfobetaine XIV has no isobestic point, but only intersection points of the curves in pairs, which indicates a multicomponent character of the system [9]. The numerical values of pK_a were determined according to the formula:

$$pK_a = pH + \lg\frac{D_A - D}{D - D_{HA}},$$

where D_A and D_{HA} are optical densities of a solution containing only an A or HA form, D is the optical density of the solution at an intermediate pH value [9].

The pK_a values found are higher than those in compounds without a $CH_2SO_3^-$ group [10, 11] (Table 1). This can be also explained by lower planarity of the molecules of compounds that we synthesized, which hinders the intramolecular charge transfer from the phenol group to the pyridinium ring and increases the negative charge on the phenol group oxygen atom.

The structure of the compounds obtained was confirmed by UV, IR, and PMR spectra (Tables 1 and 2). In the IR spectra of all the compounds there are absorption bands at 1050-1015 and 1190-1150 cm^{-1} related to the stretching vibrations of the sulfo group S=O, while for compounds II, III, X-XXIII there are overlapping bands in the 1645-1600 cm^{-1} region, which can be related to both the ethylene bond $\nu(C{=}O)$ and the $\nu(C{=}\overset{+}{N})$ bond in the pyridine ring. Elemental analysis data agreed with those calculated for compounds II and III only. Merocyanines, whose class also includes the compounds that we synthesized, can also form stable hydrates with undefined composition [12]. Therefore, for the remaining compounds a too low carbon content and an increased hydrogen content were obtained, compared with the calculated data.

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The IR spectra were run on a Specord 71-IR spectrophotometer in KBr tablets and the PMR spectra on a Hitachi R-22 spectrometer (90 MHz), using HMDS as internal standard. The UV spectra were recorded in water on a Specord UV-vis spectrophotometer. The purity of the compounds was controlled by TLC on Silufol UV-254 plates in a 2:2:1:1 ethanol–acetonitrile–chloroform–water system. To determine the pK_a, $3\cdot10^{-4}$ mole/liter solutions of sulfobetaines in water were prepared, which directly before measuring the spectra were diluted by a borate buffer to a working concentration of $6\cdot10^{-5}$ mole/liter. For each compound, the pK_a were calculated with respect to two series of optical densities, measured at λ_{max} of the two conjugate forms.

2-(4-Styrylpyridinio)ethanesulfonate (II). A. A mixture of 4.02 g (20 mmoles) of 2-(4-methylpyridinio)ethanesulfonate (I) [13], 3.18 g (30 mmoles) of benzaldehyde, 100 ml of absolute ethanol and 2 ml of piperidine was stirred for 12 h at 80°C. It was then cooled to 20°C, the crystals were filtered, dried in a vacuum-desiccator, and recrystallized from 85% aqueous ethanol. Yield, 4.2 g. Found, %: C 62.5; H 5.4; S 10.8. $C_{15}H_{15}NO_3S$. Calculated, %: C 62.3; H 5.2; S 11.1.

B. A solution of 6.7 g (37 mmoles) of 4-styrylpyridine and 7.8 g (37 mmoles) of sodium β-bromoethanesulfonate in 80 ml of ethylene glycol was boiled for 10 h. The mixture was cooled to 20°C, the crystals were filtered, washed with ether, and dried in a vacuum-desiccator. Yield, 5.8 g. Samples of sulfobetaine II, synthesized by methods A and B were identical in their IR spectra.

3-(4-Styrylpyridinio)propanesulfonate (III). A solution of 4.53 g (25 mmoles) of 4-styrylpyridine and 3.06 g (25 mmoles) of propane sultone in 50 ml of acetonitrile was boiled with stirring for 8 h. The solution was evaporated, and the residue was recrystallized from ethanol. Yield, 5.49 g. Found, %: C 63.1; H 5.7; S 10.0. $C_{16}H_{17}NO_3S$. Calculated, %: C 63.3; H 5.6; S 10.6.

2-(1-Ethyl-4-pyridinio)ethanesulfonate (VII). A solution of 8.4 g (40 mmoles) of sodium 2-(4-pyridyl)ethanesulfonate (V) and 6.53 g (60 mmoles) of ethyl bromide in a mixture of 10 ml of acetonitrile and 15 ml of water was stirred for 12 h at 40°C. The solution was then evaporated in vacuo, the residue was dissolved in 20 ml of concentrated HCl, and the undissolving sodium bromide was filtered. The filtrate was evaporated in vacuo, and the residue recrystallized from ethanol. Yield, 6.2 g (72%); mp, 229-230.5°C. PMR spectrum: 8.66 (2H, d, 2H-Py); 7.90 (2H, d, 3H-Py); 4.53 (2H, q, $CH_2\overset{+}{N}$); 3.29 (4H, s, CH_2CH_2); 1.56 (3H, t, CH_3).

Sulfobetaines VIII, IX were synthesized by the method in [14].

3-(4-Hydroxyphenyl)-2-(4-pyridinio)-2-propenesulfonate (X). A mixture of 5.24 g (28 mmoles) of 2-(4-pyridyl)ethanesulfonic acid (VI) [15], 4.9 g (40 mmoles) of 4-hydroxybenzaldehyde, 3 ml (30 mmoles) of piperidine, and 30 ml of absolute DMSO was stirred at 110° to complete dissolution of VI (~12 h). Dimethyl sulfoxide was evaporated in vacuo, and the residue was chromatographed on a column with silica gel (acetonitrile–water, 5:1). Yield, 0.41 g.

Sulfobetaine XI was obtained in a similar way.

3-(4-Hydroxyphenyl)-2-(1-ethyl-4-pyridinio)-2-propenesulfonate (XII). A mixture of 10.8 g (50 mmoles) of sulfobetaine VII, 7.4 g (60 mmoles) of 4-hydroxybenzaldehyde, 3 ml (30 mmoles) of piperidine, 40 ml of absolute ethanol and 10 ml of absolute DMSO was vigorously stirred at 80°C to complete dissolution of VII (~5 h). The solution was evaporated to half of its volume, the crystals that separated were filtered, washed with water, and recrystallized from 85% aqueous ethanol. Yield, 6.7 g.

Styrylpyridiniosulfobetaines XIII-XXI were synthesized in a similar way. Compound XV was purified by crystallization from a 5:1 acetonitrile–water mixture, sulfobetaine XIV — by chromatography on a column, similarly as in the case of X.

Sodium 3-(4-hydroxyphenyl)-2-(1-ethyl-4-pyridinio)-2-propenesulfonate (XXII). Water was evaporated in vacuo at 50°C from a solution of 4.8 g (15 mmoles) of sulfobetaine XII and 0.64 g (16 mmoles) of sodium hydroxide in 30 ml of water. The residue was recrystallized from 85% aqueous ethanol. Yield, 4.9 g.

Compound XXII was synthesized in a similar way.

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ACID HYDROLYSIS OF N-METHYL DERIVATIVES OF 4-PHENYL-5-OXO-4,5-DEHYDROINDENO[1,2-b]PYRIDINE

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The splitting of the dihydropyridine ring of N-methyl-substituted 4-phenyl-5-oxo-4,5-dihydroindeno[1,2-b]pyridine in an acid medium takes place at the C—N bond. During the splitting of 1,2-dimethyl-4-phenyl-4,5-dihydroindeno[1,2-b]-pyridine, 4-phenyl-4-(indane-1,3-dion-2-yl)butan-2-one is formed, while in the case of the 3-ethoxycarbonyl derivative of indenopyridine, together with the Michael retroreaction leading to 2-benzylideneindane-1,3-dione, a recyclization of the intermediate product into a derivative of dihydroindeno-2-pyridone takes place.

It is known [1] that during alkylation, 5-oxo-1H-4,5-dihydroindeno[1,2-b]pyridines form C- and N-alkylation products, i.e., they exhibit properties characteristic of enamino ketones In the present work, it was shown that splitting of the dihydropyridine ring of 1,2-dimethyl-4-phenyl-5-oxo-4,5-dihydroindeno[1,2-b]pyridine (Ia) and its 3-ethoxycarbonyl derivative (Ib) in an acid medium proceeds as an acid hydrolysis of enamines.

According to the generally accepted scheme, the hydrolysis of enamines includes the protonation of the β-carbon atom, followed by the addition of water to the α-carbon atom and cleavage of the C—N bond. Since the molecule of dihydroindenopyridine I contains two fragments, which are enamine systems: $C_{(4a)}$—$C_{(9b)}$—N and $C_{(3)}$—$C_{(2)}$—N, a cleavage of both the N—$C_{(9b)}$ and N—$C_{(2)}$ bond is possible with the formation of intermediate products A and B. However, these primary hydrolysis products were not detected in the reaction mixture, but products of their further transformation were isolated. Thus, during the hydrolysis of 1,2-dimethyl-3-ethoxycarbonyl-4-phenyl-5-oxo-4,5-dihydroindeno[1,2-b]pyridine (Ib), 2-benzylideneindane-1,3-dione (II), 2-benzylindane-1,3-dione (III), and 1-methyl-3-acetyl-4-phenyl-2,5-dioxo-2,5-dihydroindeno[1,2-b]pyridine (IV) were detected. Indenopyridone IV is an oxidized form of 1-methyl-3-acetyl-4-phenyl-2,5-dioxo-2,3,4,5-tetrahydroindeno[1,2-b]pyridine (V), formed as the result of an intramolecular interaction of an ester group with the 1-methylamino functional group of the intermediate product B. Structure IV was confirmed by spectral methods and alternative synthesis: cyclization of N-monomethyl α-acetyl-β-phenyl-β-(indane-1,3-dion-2-yl)propionamide (VI) into 2,5-dioxo-2,3,4,5-tetrahydroindenopyridine

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