E-(20S)-3β-Acetoxy-24-acetoxyiminocholest-5,22-dien-20-ol (Vb, $C_{31}H_{47}NO_5$). Prepared in an analogous manner from 0.215 g (0.5 mmole) enoxime IVb in a yield of 0.216 g (84%).

LITERATURE CITED

1. A. A. Akhrem, F. A. Lakhvich, and V. A. Khripach, *Khim. Geterotsikl. Soedin.*, No. 9, 1155 (1981).
2. A. A. Akhrem, V. A. Khripach, F. A. Lakhvich, M. I. Zavadskaya, O. A. Drachevnova, and I. A. Zorina, *Dokl. Akad. Nauk SSSR*, **297**, 364 (1987).
3. A. A. Akhrem, V. A. Khripach, R. P. Litvinovskaya, A. V. Baranovskii, and E. V. Borisov, Abstracts of Proceedings, 12th International Conference on Isoprenoids, Beijing (1987), p. 22.
4. F. A. Lakhvich, T. V. Yankova, E. V. Koroleva, and A. A. Akhrem, *Khim. Geterotsikl. Soedin.*, No. 12, 1698 (1987).
5. K. Kihira, Y. Morioka, and T. Hoshita, *J. Lipid. Res.*, **22**, 1181 (1981).
6. V. Jager and N. Grund, *Angew. Chem.*, **88**, 27 (1976).
7. G. Timms and E. Wildsmith, *Tetrahedron Lett.*, 195 (1971).

SYNTHESIS OF (–)-(4R,5R)- AND (+)-(4S,5S)-1-ALKYL-4-(4'-NITROPHENYL)-1-AZONIUM-3,7-DIOXABICYCLO[3.3.0]OCTANE HALIDES

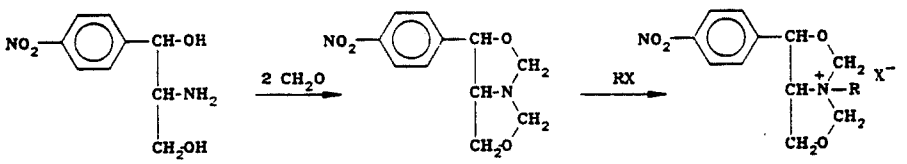
V. P. Zaitsev, P. P. Purygin, and S. Kh. Sharipova

UDC 547.787.3'435.22.07

A preparative method has been proposed for the synthesis of bicyclic quaternary ammonium salts via sequential treatment of (–)-(1R,2R)- and (+)-(1S,2S)-1-(4'-nitrophenyl)-2-amino-1,3-propanediol with paraform followed by an alkyl halide.

Quaternary ammonium salts can be used as phase transfer catalysts [1-3], orientation directing agents as additive for liquid crystals [4], as well as growth-regulating substances [5], general antiseptics [6, 7], and as agents with curarelike activity [6, 8].

We have now prepared two series of salts (Table 1) from (–)-(1R,2R)- and (+)-(1S,2S)-1-(4'-nitrophenyl)-2-amino-1,3-propanediol [(–)-I and (+)-I, respectively] using a two-step reaction sequence:



(+)-I or (–)-I (+)-II or (–)-II (+)-III or (–)-III

a RX=CH_3I, b RX=C_2H_5Br, c RX=$C_6H_5CH_2Cl$, d RX=$C_6H_5CH_2Br$, e RX=CH_2=CH—CH_2Cl, f RX=CH_2=CH—CH_2Br

Kuibyshev State University, Kuibyshev.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1394-1395, October, 1990. Original article submitted February 13, 1989; revision submitted November 24, 1989.

0009-3122/90/2610-1162$12.50

TABLE 1. Physical Chemical Characteristics of Compounds (+)-IIIa-f

Compound	Empirical formula	R	T, °C	$[\alpha_D]$, deg in alcohol	Yield, %
IIIa	$C_{12}H_{15}IN_2O_4$	CH_3	183...185	+23	95
IIIб	$C_{13}H_{17}BrN_2O_4 \cdot H_2O$	C_2H_5	83...85	+33	40
IIIв	$C_{18}H_{19}ClN_2O_4 \cdot H_2O$	$C_6H_5CH_2$	165...166	+101	42
IIIг	$C_{18}H_{19}BrN_2O_4$	$C_6H_5CH_2$	184...185	+92	45
IIIд	$C_{14}H_{17}ClN_2O_4 \cdot H_2O$	$CH_2=CH-CH_2$	89...92	+49	30
IIIe	$C_{14}H_{17}BrN_2O_4 \cdot H_2O$	$CH_2=CH-CH_2$	84...86	+43	89

*For compounds prepared from (–)-I, their mp and $[\alpha]_D$ values were superimposable on the above-reported values, and they were not subjected to elemental analysis.

Compounds III, with the exception of IIIa, were isolated in the form of monohydrate crystals, which lost the water of hydration upon prolonged storage.

EXPERIMENTAL

The results of C and H elemental analysis agreed with calculations.

(+)-(4S,5S)-1-(4'-Nitrophenyl)-1-aza-3,7-dioxabicyclo[3.3.0]octane [(+)-IIa]. To a flask fitted with a Dean–Stark trap was charged 42.5 g (0.2 moles) compound (+)-I and 16 g (0.53 moles) paraform in 100 ml benzene; the reaction mixture was refluxed for 2 h, filtered, and the benzene distilled off until a viscous mass remained, which crystallized upon standing. Compound (+)-II was used without further purification in subsequent experiments. Yield 95%, mp 75-77°C. According to the literature [9], mp 79°C.

(+)-(4S,5S)-1-Methyl-4-(4'-nitrophenyl)-1-azonium-3,7-dioxabicyclo[3.3.0]octane Iodide [(+)-IIIa]. To compound (+)-II, dissolved in acetone, was added a threefold excess of methyl iodide, and the resulting mixture was allowed to stand overnight. Compound (+)-(IIIa) was removed by filtration, washed with acetone on the filter, and dried.

(+)-(4S,5S)-1-Benzyl-4-(4'-nitrophenyl)-1-azonium-3,7-dioxabicyclo[3.3.0]octane Chloride Monohydrate [(+)-IIIc]. To compound (+)-II, dissolved in acetone, was added a threefold excess of benzyl chloride, and the resulting mixture was refluxed for several hours on a water bath. The resulting crystals of compound (+)-IIIc were removed by filtration, washed with acetone and alcohol on the filter, and recrystallized from alcohol.

LITERATURE CITED

1. L. A. Yanovskaya and S. S. Yufit, *Organic Synthesis in Two-Phase Systems* [in Russian], Khimiya, Moscow (1982), p. 184.
2. W. Weber and G. Gokel, *Phase Transfer Catalysis in Organic Synthesis* [Russian translation], Mir, Moscow (1980), p. 327.
3. V. M. Potapov, *Itogi Nauki i Tekhniki, Ser. Org, Khim.*, Vol. 4, VINITI, Moscow (1984), p. 3.
4. E. S. Luk'yanchenko, V. A. Kozunov, and V. I. Grigos, *Usp. Khim.*, **54**, 214 (1985).
5. Yu. A. Baskakov, *Zh. V. Khim. O.*, **29**, 22 (1984).
6. G. Dayson and P. May, *Chemistry of Synthetic Pharmaceutical (Medicinal) Agents* [Russian translation], Mir, Moscow (1964), p. 659.
7. B. N. Stepanenko, T. S. Ulitina, and V. V. Zelenkova, *Khim. Farm. Zh.*, **8**, 21 (1974).
8. M. V. Rubtsov and A. G. Baichikov, *Synthetic Chemical Pharmaceutical Agents* [in Russian], Meditsina, Moscow (1971), p. 328.
9. W. H. Edgerton, J. R. Fischer, and G. W. Moersch, *J. Am. Chem. Soc.*, **79**, 6487 (1957).